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Naval Fuels and Fuel Cells

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Fuels for Naval Applications

- Requirements
  - world wide operation
  - infrastructure
  - low cost
  - ship / fleet wide operation
  - Replenishment at Sea
  - Use in fuel cells / reformers
- Potential Future Fuels
  - Marine Diesel
  - Synthetic fuel
  - Gas (LPG, LNG)
  - Methanol
  - Hydrogen

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Future Fuels - Diesel

- Marine Diesel and Marine Aviation fuels
  - Currently F-76, F-44, MGO
  - predictions for >50 years supply
  - move to single fuel ? (on carriers)
  - move to low sulphur , low aromatics etc
  - change will be gradual , depends on legislation world wide
  - as energy source for fuel cells needs complex fuel reformer

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Future Fuels - Synthetic

- Synthetics
  - made from syngas, coal, shale, natural gas
  - low (no) sulphur, low aromatics
  - fuel quality can be made to order
  - huge reserves of gas, shale etc
  - compatible with IC engines
  - already in use in aviation fuel
  - production very small at present , just gearing up
  - fuel cell version ?

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Liquid fuel reformation

- Reformation
  - easier to store liquid fuels
  - reformation requires extra oxygen
- Complicated reformer is required to convert fuel to H_2 supply
- Will produce CO_2 by-product
- For submarine applications use steam reforming
  - lower oxygen demand
  - higher efficiency

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Future Fuels - Gas

- LPG, CNG
  - + Huge reserves
  - + easy to reform
  - + internal reforming Solid Oxide Fuel Cell

  - – little infrastructure or world wide availability
  - – Safety on board
  - – Replenishment at Sea a problem

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Future Fuels - Hydrogen

storage & production methods

- Physical methods
  - Compressed gas
  - Cryogenic liquid
  - Metal hydrides
  - Carbon adsorbants
- Chemical methods
  - Hydride hydrolysis
  - Ammonia borane

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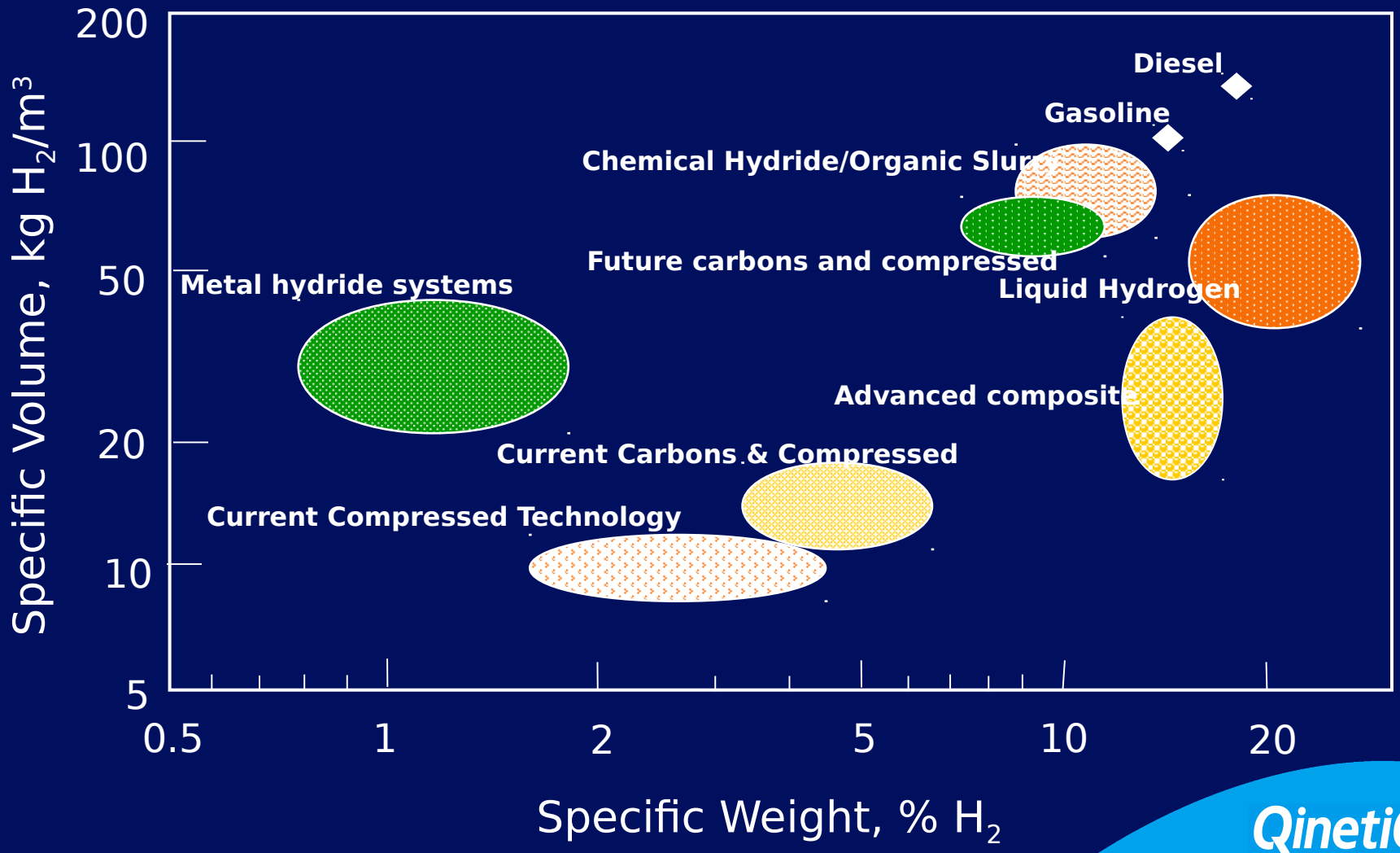
Summary of Hydrogen Storage



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Compressed gas

- Traditional steel cylinders
  - heavy,
  - poor energy density.
- Composite cylinders
  - Lightweight cylinders - carbon fibre wrapped over an inner Al or thermoplastic liner.
  - much lighter than steel cylinders.
  - 700 bar, 11 % by weight.
- Bulky storage method.

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Liquid Hydrogen

- Low temperature, -253◦C @ 1 atmosphere
- Special very well insulated containers are needed
- Less of 0.2 - 3 % per day from natural boil off
- 13-20 wt.% Hydrogen Storage
- Less efficient for smaller systems
- Energy intensive needs 40 % of energy for liquefaction

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Metal hydrides

- Good volumetric performance
  - theoretical 100 g/L, 1860 Wh/L
- Poorer gravimetric performance
  - theoretical 2 wt %, 370 Wh/kg
- Desorption endothermic - requires heat
- H_2 stored at constant pressure - safe

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Carbon nanofibres

- Early development stage
- Nanofibres consist of stacked graphite plates
- Thin fibres of 5-100 nm diameter and 5-100 μm length
- Spacing between planes perfect for H_2
- Potentially store high level of hydrogen
- Modelling suggests that large H_2 storage capacities are possible
- Still much scepticism

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Royal Navy Requirement for Alternative Power Sources

- Royal Navy Marine Engineering Development Strategy Paper endorsed the full electric ship.
- Alternative clean power sources are required to meet the power generation requirement.
- The potential benefits of fuel cells:-
  - Reduced signature
  - Reduced noxious emissions
  - Reduced repair/maintenance

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Fuel Cell Fuel Constraints

- Fuel cells require hydrogen for power generation.
- The storage of hydrogen on board ship would pose significant safety and practical problems.
  - Explosive Hazard
  - Bulky Storage Vessels
- Hydrogen must be derived from NATO Logistic Fuels:-
  - AVCAT F-44
  - DIESO F-76
  - Marine Gas Oil (MGO)

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Benefits and Problems Associated with Logistic Fuels

- Benefits
  - Supply network exists
  - Fuel requirement common to existing systems (gas turbines will still be operated initially)
- Problems
  - Additional equipment required to reform fuel
  - Cannot guarantee fuel quality (must develop fuel reformer to operate with worst case fuel)
  - Sulphur removal, Soot formation, Carbon monoxide removal

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Composition of NATO Logistic Fuels

- AVCAT F-44
  - average composition $C_{9.32}H_{18.06}$
  - H/C ratio 1.94
  - up to 0.3 % sulphur compounds
- Dieso F-76
  - average composition $C_{13.93}H_{22.62}$
  - higher in aromatics and heavy hydrocarbons
  - more prone to cause soot formation
  - H/C ratio 1.62
  - up to 1 % sulphur compounds
- Marine Gas Oil (MGO)
  - Composition varies dependent on source (at best diesel quality)
  - up to 1% sulphur compounds

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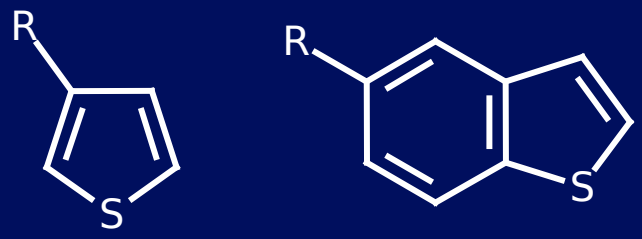
Pre-reformation Fuel Treatment

- Before the fuel can be reformed it requires a two-stage treatment process
- Contaminants ingested in storage tanks
  - Salt from sea water used as ballast - Could cause corrosion
  - Particulate debris (flakes of paint, rust etc) - Could cause blockages in reformer system
- Logistic Fuels contain up to 1% by weight of organosulphur compounds.
  - Thiols, Sulphides, Thiophenes, Benzothiophenes



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Sulphur Removal

- Fuel cells are intolerant of hydrogen sulphide and organosulphur compounds
- Catalysts used in fuel processing may also be sulphur intolerant (sulphur tolerant catalysts being researched)
- Two stage removal process:-
  - Organosulphur compounds reacted with hydrogen over catalyst (typically cobalt/nickel molybdates) to form hydrogen sulphide.
  - Hydrogen sulphide removed by absorption (typically onto zinc oxide)
  - $ZnO + H_2S \Leftrightarrow ZnS + H_2O$

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Reforming Process

- Fuel reforming is fundamentally the chemical breakdown of hydrocarbons into hydrogen and oxides of carbon.
  - $C_n H_{2n+2} + nO_2 \longrightarrow n+1\ H_2 + nCO_2$ (Ideal reaction)
- Due to the complex mixture of hydrocarbon molecules within NATO Logistic Fuels complete conversion is not achieved
  - Incomplete Carbon Combustion gives Carbon Monoxide, low chain hydrocarbons and methane.

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Methods of Reforming

- Four main Fuel Reforming Processes
  - Steam Reforming (QinetiQ ARTD)
  - Partial Oxidation (POX)
  - Autothermal
  - Plasma Reforming (Massachusetts Institute of Technology Plasmatron)

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Steam Reforming

$$C_nH_m + 2n\,H_2O \longrightarrow (m/2 + 2n)\,H_2 + n\,CO_2$$

- Reaction temperature is 650-850 ºC
- Reaction is strongly endothermic (Requirement for steam reduces electrical efficiency)
- Better H_2 yield than Partial Oxidation (POX)
- Reaction Produces ~70% H_2, 20% CO_2, and ~2% CO
- Additional gas clean-up stages required (Water gas shift reactors)
- Reactor systems are complex and bulky

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Partial Oxidation

$$C_nH_m + n/2\ O_2 \longrightarrow n\ CO + m/2\ H_2$$

- Reaction is strongly exothermic
- Lower H_2 yield than steam reforming
- Quicker start-up than steam reformation
- Additional water gas shift reactors will improve hydrogen yield

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Incomplete Fuel Conversion

- The complex mixture of hydrocarbon molecules within NATO Logistic Fuels means complete conversion to carbon dioxide and hydrogen is not achieved
  - Incomplete Carbon Combustion gives low chain hydrocarbons, methane and Carbon Monoxide.

$$C_nH_{2n+2} + \tfrac{1}{2}nO_2 \longrightarrow n+1\ H_2 + nCO$$

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Reformate gas clean-up

- Carbon Monoxide is a Fuel Cell poison and requires removal
  - water-gas shift reactions (also increases hydrogen yield) at high and low temperatures
  - selective oxididation (converts residual CO to CO_2)

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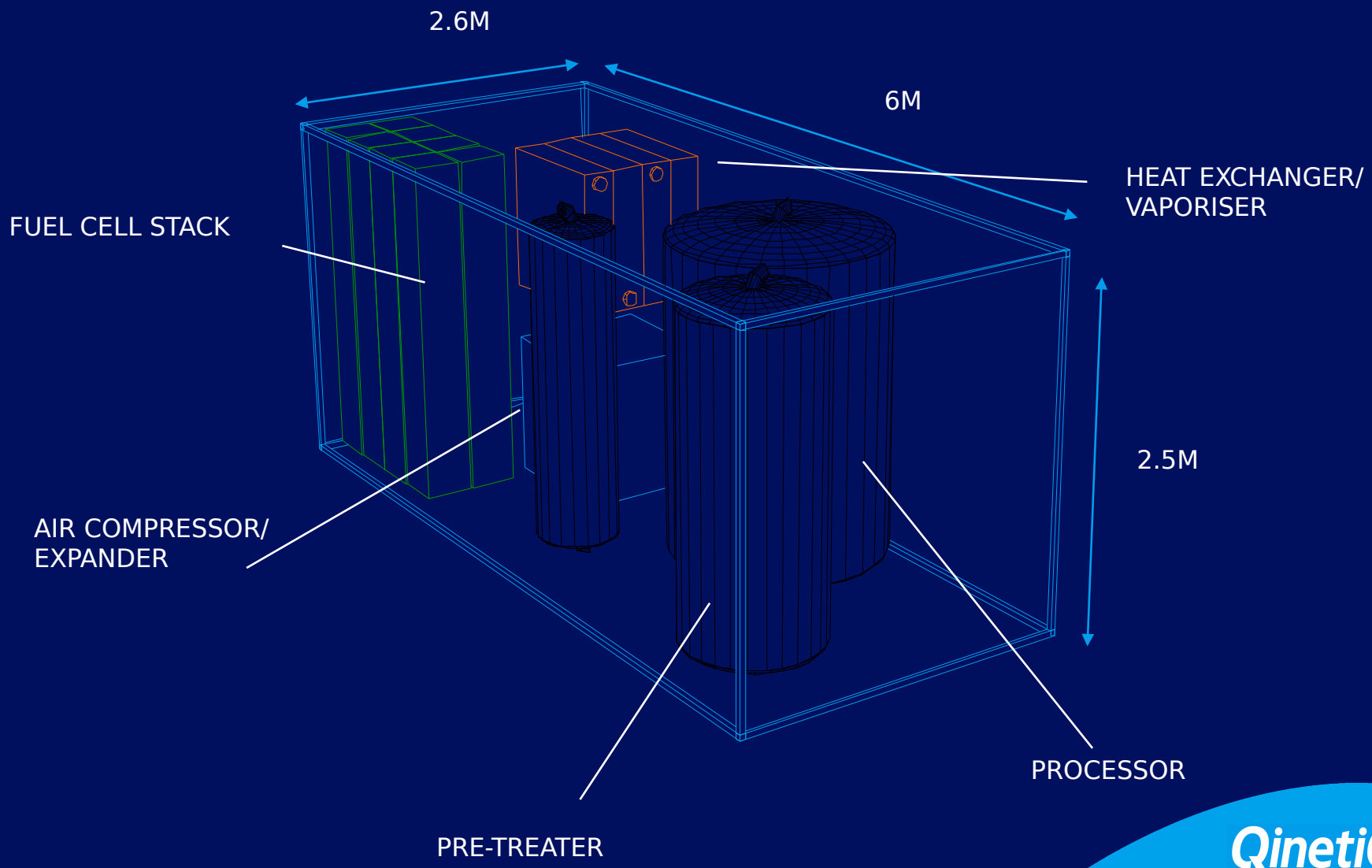
Volume Constraints



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Solid Polymer Fuel Cells

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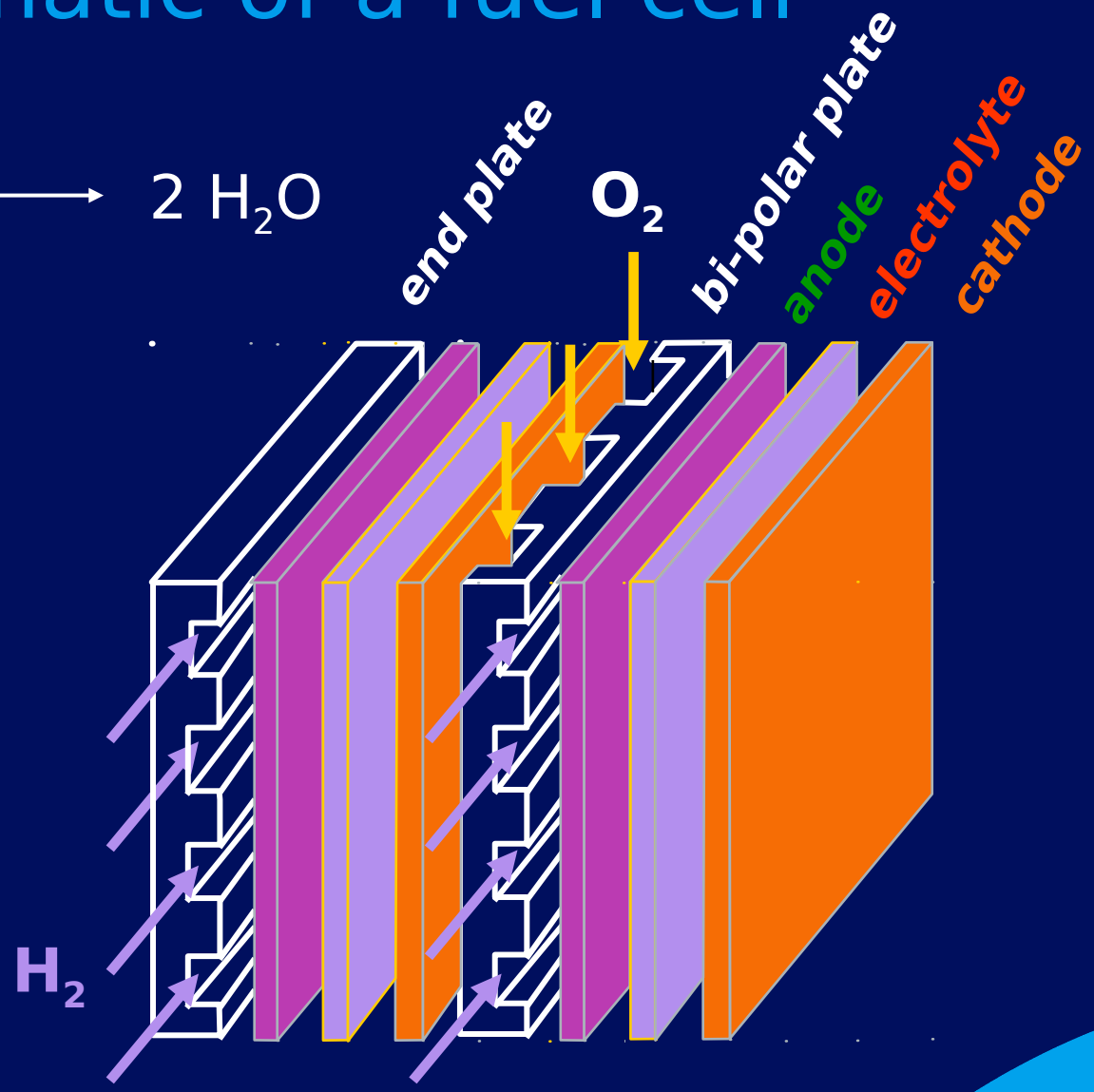
Schematic of a fuel cell

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$



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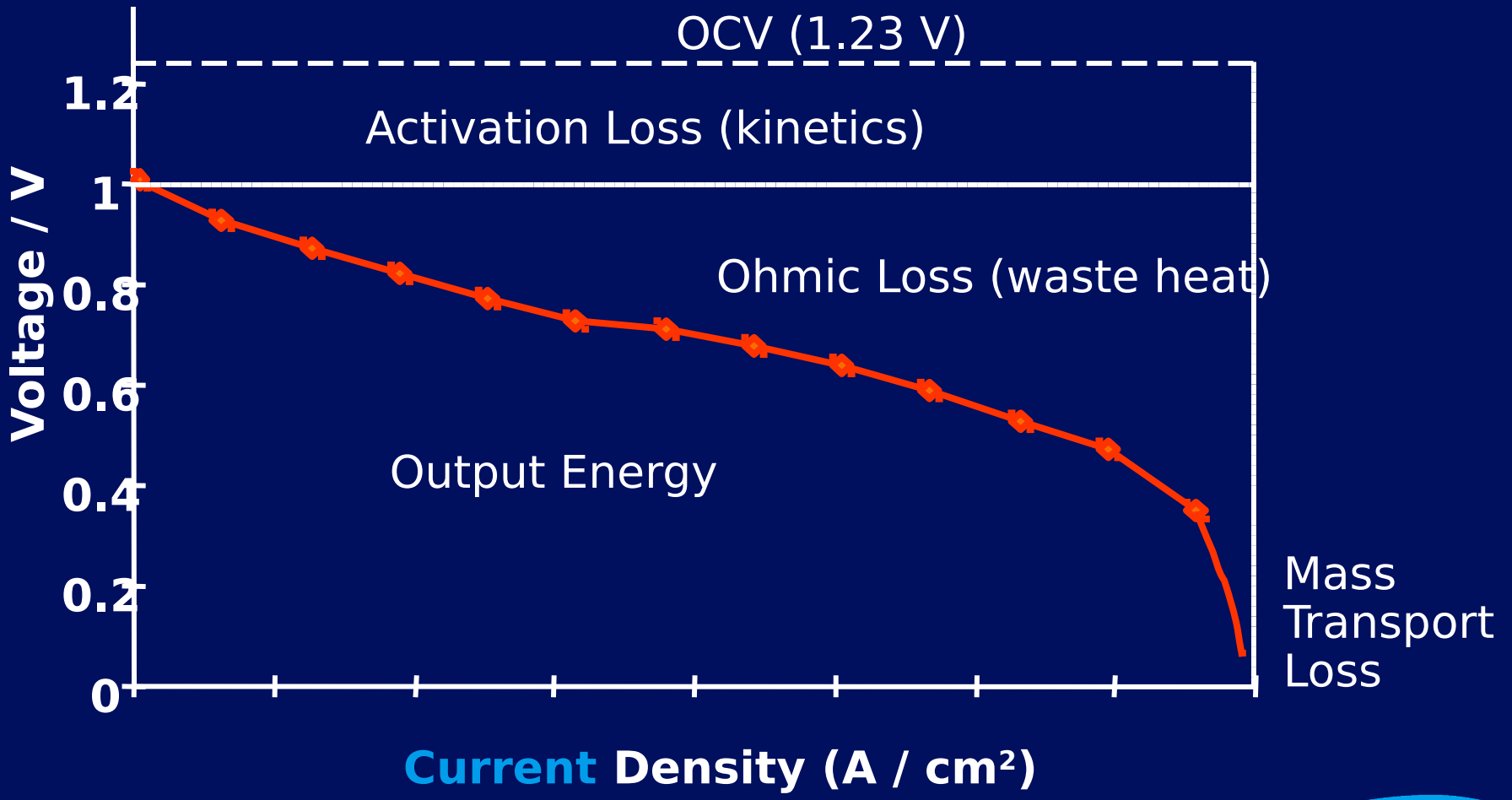
Fuel cell performance



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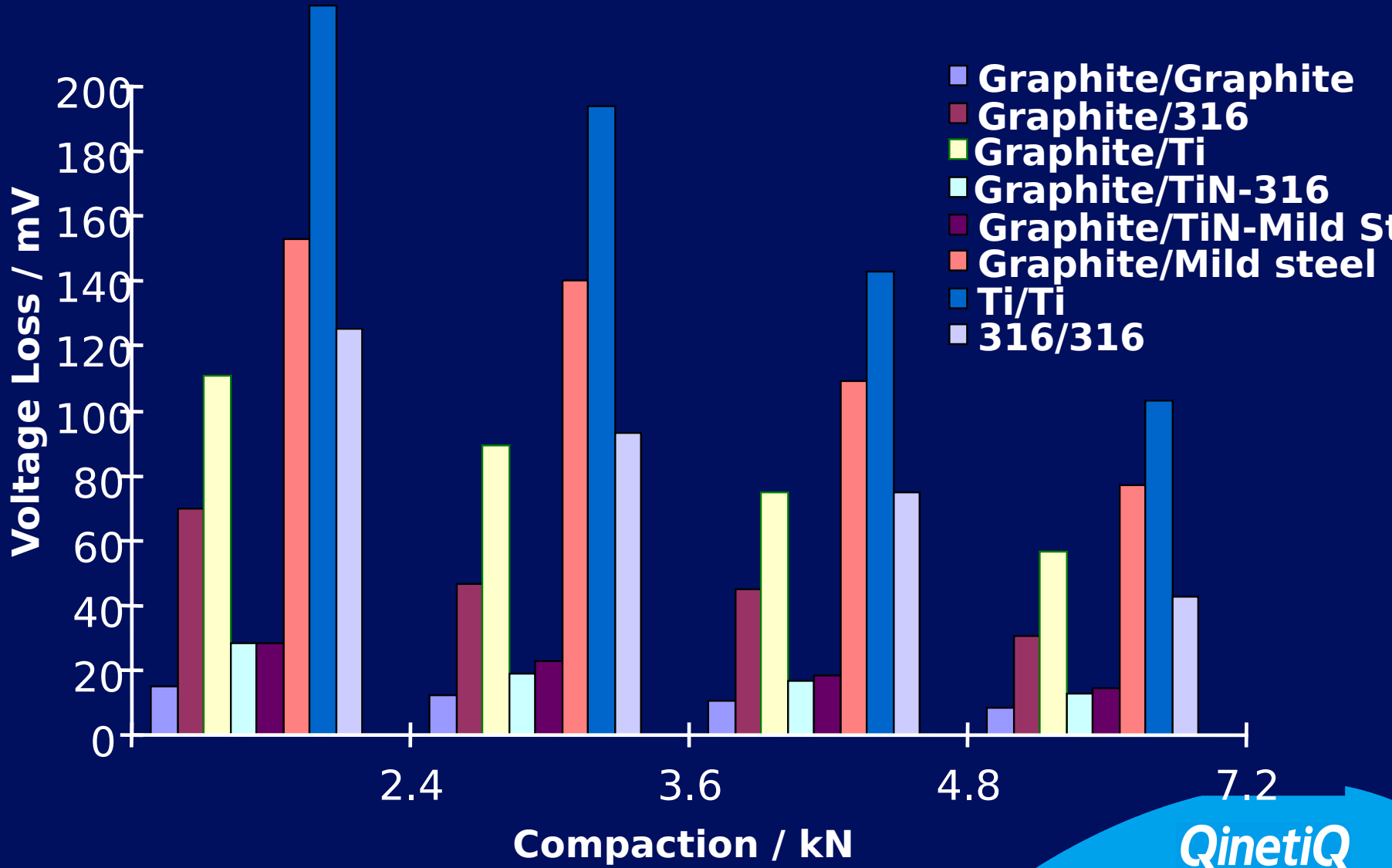
Voltage loss at 20A from interfacial resistance



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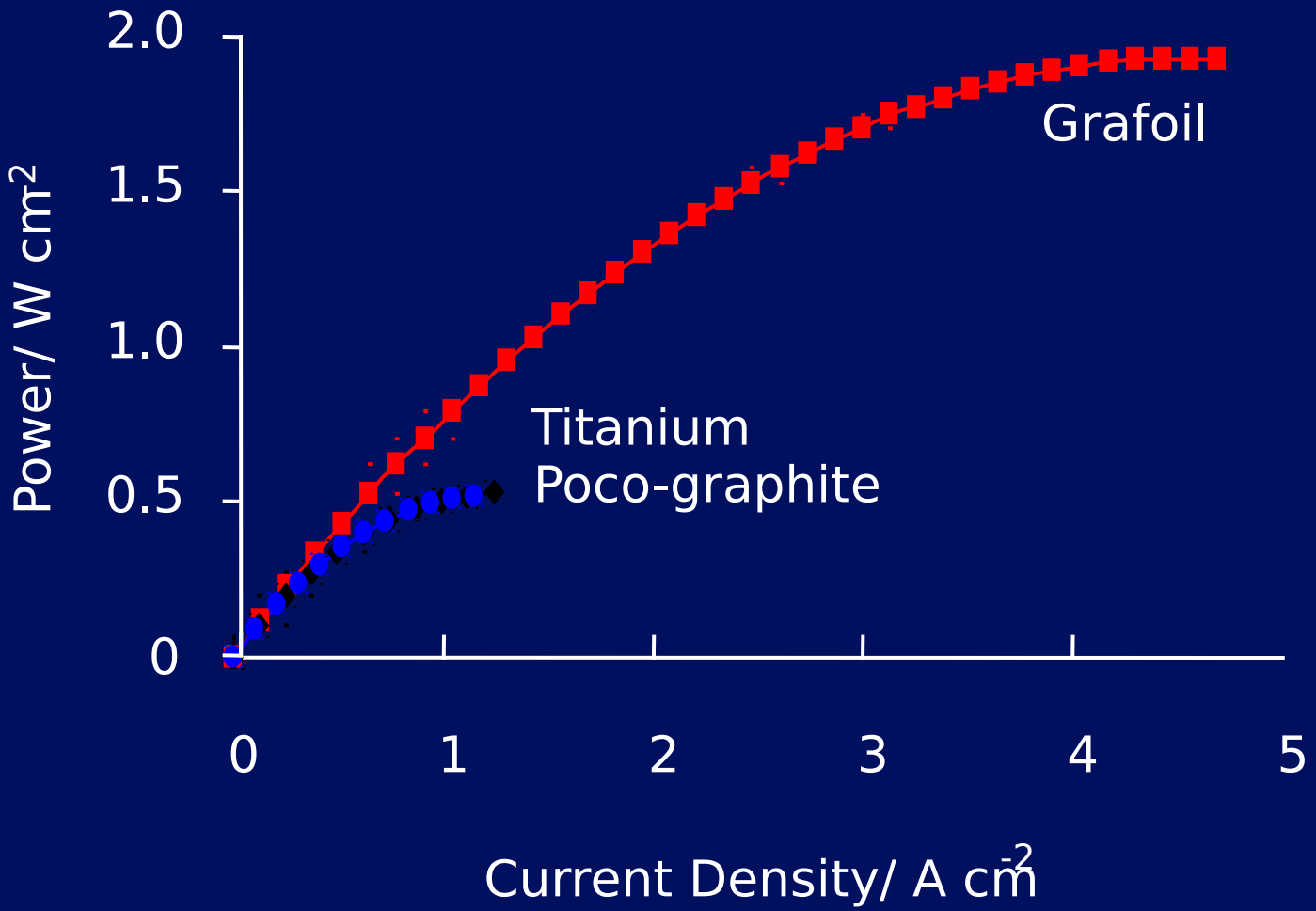
Performance comparison of materials



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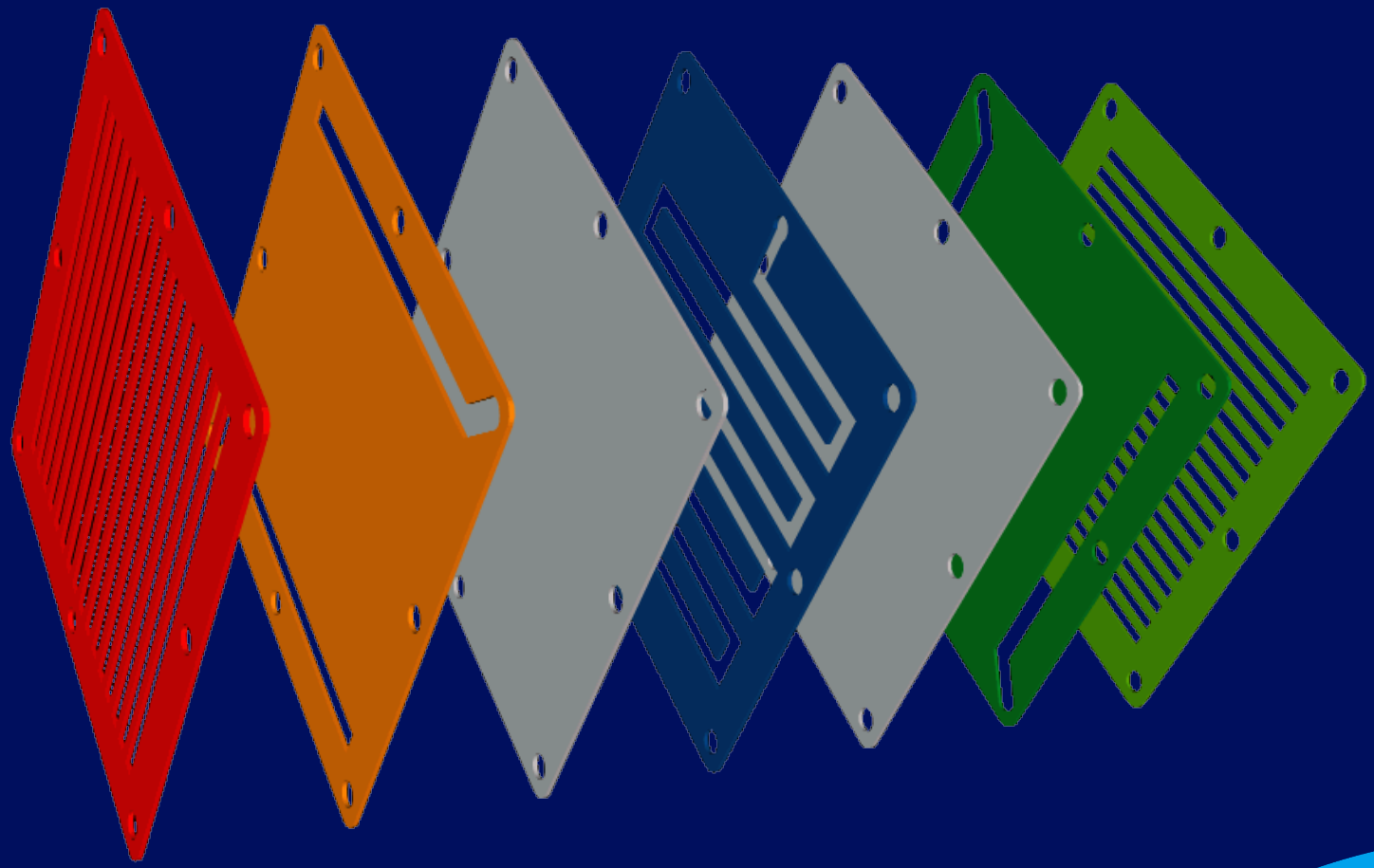
Construction of titanium bipolar plate from multiple foils



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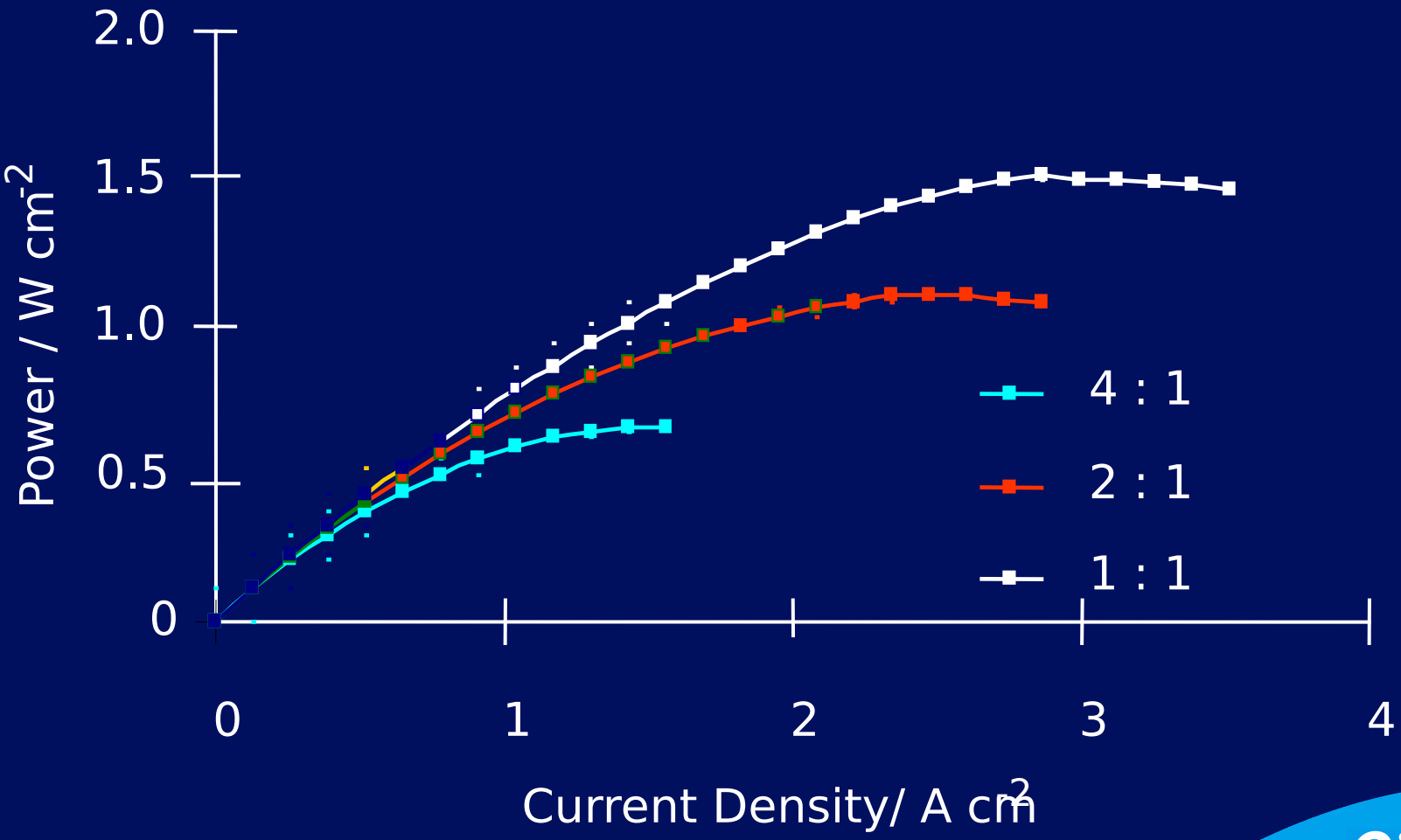
Effect of changing channel width on a grafoil single cell



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